

WE CLAIM:

1. A method of selectively depositing a layer on a substrate comprising a first surface and a second surface, the method comprising:  
modifying the first surface; and  
selectively depositing a layer on the second surface relative to the first surface using an atomic layer deposition (ALD) process, wherein modifying the first surface blocks deposition by the ALD process.
2. The method of Claim 1, wherein modifying the first surface comprises adsorption of a blocking substance that blocks growth by atomic layer deposition.
3. The method of Claim 2, further comprising removing the blocking substance from the first surface after selectively depositing the layer.
4. The method of Claim 1, wherein modifying the first surface comprises forming growth-blocking ligands on the first surface.
5. The method of Claim 4, wherein the growth-blocking ligands have the chemical formula  $\text{SiX}_n$ , where X is selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) and n is an integer selected from the group consisting of 1, 2 and 3.
6. The method of Claim 1, further comprising conditioning the second surface prior to modifying the first surface.
7. The method of Claim 1, further comprising conditioning the second surface after modifying the first surface and prior to selectively depositing the layer.
8. A method of selectively depositing a layer on a substrate comprising:  
modifying a first surface of the substrate to prevent subsequent deposition of the layer thereon; and  
selectively coating over a second surface of the substrate as compared to the first surface by repeatedly alternating exposure of the substrate to at least two reactants, each alternating exposure having a self-limiting effect.
9. The method of Claim 8 wherein the first surface comprises a conductor and the second surface comprises an insulating material that is selectively coated.

10. The method of Claim 9, wherein the second surface defines an opening in an insulating layer within an integrated circuit and the first surface comprises a metal element exposed by the opening.

11. The method of Claim 9, wherein selectively coating comprises depositing a barrier material over the insulating material.

12. The method of Claim 11, wherein the barrier material is conductive and has a resistivity less than about 300  $\mu\Omega$ -cm.

13. The method of Claim 11, wherein the barrier material comprises a metal nitride.

14. The method of Claim 13, wherein the barrier material comprises titanium nitride.

15. The method of Claim 11, wherein the barrier material is an insulator.

16. The method of Claim 8, wherein modifying comprises forming a growth-blocking layer on the first surface.

17. The method of Claim 16, wherein the growth blocking layer is selectively removed after coating the second surface and prior to further deposition.

18. The method of Claim 8, wherein modifying comprises forming ligands on the first surface and the second surface and subsequently converting the ligands on the first surface into a growth-blocking layer.

19. The method of Claim 8, wherein modifying comprises forming a sacrificial layer on the first surface.

20. The method of Claim 19, wherein the sacrificial layer comprises a material susceptible to etching from exposure to the at least two reactant fluids.

21. A method of selectively blocking formation of a thin film by an atomic layer deposition (ALD) process on a first surface compared to a second surface comprising:

selectively modifying the first surface; and

alternatingly contacting the first and second surfaces with vapor-phase reactants to selectively deposit a material over the second surface relative to the first surface in an atomic layer deposition (ALD) process.

22. The method of Claim 21, wherein modifying comprises forming a growth-blocking layer over the first surface.

23. The method of Claim 21, wherein modifying comprises a physical modification.

24. The method of Claim 21, wherein modifying comprises a chemical modification.

25. The method of Claim 24, wherein modifying comprises oxidation.